

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : D21H 19/00, 23/50, B05D 1/00, 7/06		A1	(11) International Publication Number: WO 97/36049
			(43) International Publication Date: 2 October 1997 (02.10.97)
(21) International Application Number: PCT/NL97/00149		(81) Designated States: AL, AU, BA, BB, BG, BR, CA, CN, CU, CZ, EE, GE, HU, IL, IS, JP, KP, KR, LC, LK, LR, LT, LV, MG, MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, TR, TT, UA, US, UZ, VN, YU, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).	
(22) International Filing Date: 24 March 1997 (24.03.97)			
(30) Priority Data: 96200819.9 26 March 1996 (26.03.96) EP			
(34) Countries for which the regional or international application was filed: NL et al.			
(71) Applicants (for all designated States except US): DSM N.V. [NL/NL]; Het Overloon 1, NL-6411 TE Heerlen (NL). MICHAEL HUBER MÜNCHEN GMBH [DE/DE]; Heimstetten, Feldkirchener Strasse 15, D-85551 Kirchheim (DE).		Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
(72) Inventors; and			
(75) Inventors/Applicants (for US only): MISEV, Tosko, Alexander [NL/NL]; Rengersdiep 6, NL-8032 NK Zwolle (NL). STEEMAN, Paulus, Antonius, Maria [NL/NL]; Holsterbeek 6, NL-6166 JR Geleen (NL). SCHULZE-HAGENEST, Detlef [DE/DE]; Am Hermannholz 9, D-85630 Grasbrunn (DE). HUBER, Burkard [DE/DE]; Ludwigsweg 5, D-85551 Kirchheim (DE). BUCHWEITZ, Jörg [DE/DE]; Margaretenanger 3C, D-85716 Lohhof-Unterschleißheim (DE).			
(74) Agent: SCHMEETZ, Marcel, Max, Hubertina, Johanna; Octrooibureau DSM, P.O. Box 9, NL-6160 MA Gelten (NL).			

(54) Title: PROCESS FOR COATING A BOARD- OR PAPER-LIKE SUBSTRATE WITH A POWDER PAINT COMPOSITION

(57) Abstract

The invention relates to a process for coating a board- or paper-like substrate with a powder paint composition. The powder paint particles are first charged by friction or induction in the presence of magnetic or non-magnetic particles, are next transported and are then applied to the substrate or applied to a transfer medium and subsequently transferred to the substrate, by means of an electric field between the substrate respectively the transfer medium and the means of transport whereafter the powder paint composition is cured or fused to obtain a powder coating and wherein the powder paint particles are based on solid particles of a radiation curable binder. Preferably, the substrate is paper or cardboard.

BEST AVAILABLE COPY

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakhstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

BEST AVAILABLE COPY

PROCESS FOR COATING A BOARD- OR PAPER-LIKE SUBSTRATE WITH
A POWDER PAINT COMPOSITION

5

The invention relates to a process for coating a board- or paper-like substrate with a powder paint composition.

10

In industrial applications varnishing of, for example, cellulose based sheets and webs is usually carried out using solvent or water-based varnishes. The solvent-based varnishes have as a disadvantage the evaporation of solvents into the atmosphere. Because of environmental reasons emission of solvents has to be reduced drastically. The water-based varnishes have as a disadvantage that they need much energy for drying. To achieve the highest possible gloss the use of calanders is suitable. This separate step is costly and limits the process speed.

15

20

Alternatively, liquid UV-curable varnishes are used to overcome these difficulties. However, this group of materials is often rejected because of their sensibilizing and irritating character due to the applied monomers, which are the main components of these coating liquids. Another disadvantage of this coating technology can be that the smell makes the coating unsuitable for food packaging.

25

GB-A-2056885 discloses a process for coating a cellulose fibre substrate like cardboard with a powder paint composition and curing by radiant heat. Generally a binder system for a powder paint composition consists of a resin and a crosslinker. A disadvantage of the process according to GB-A-2056885 is the limited capacity of the applied powder paint spray guns which imposes a restriction on the rate of application of powder paint to the substrate. Another disadvantage is that it is very

30

35

difficult to achieve coatings having a layer thickness below 15 μ m.

A further disadvantage is the major thermal load imposed on the heat-sensitive substrate during curing of the powder paint composition.

It is the object of the present invention to provide a process for coating a board or paper-like substrate (which substrate can already be precoated) at process speeds of substrates between, for example, 1 and 400 meter substrate/minute, giving a high quality coating with a thickness between for example 1 μ m and 100 μ m.

The invention is characterized in that powder paint particles are first charged by friction or induction in the presence of magnetic or non-magnetic particles, are next transported and then applied to the substrate, or applied to a transfer medium and are then transferred to the substrate, by means of an electric field between the substrate respectively the transfer medium and the means of transport, whereafter the powder paint composition is cured or fused into a powder coating wherein the powder paint particles are based on solid particles of a radiation curable binder system.

Suitable radiation curable binder systems include for example a polymer having unsaturated groups and a cationic curable system based on, for example epoxy resins.

Preferably, the radiation curable binder system comprises a polymer having unsaturated groups.

Preferably, said polymer having unsaturated groups has a degree of unsaturation between about 200 and about 1800 grams of polymer per mole of unsaturated group.

Charging of the powder paint particles by friction or induction, transport or conveying and application to the substrates can be effected using processes commonly known in photocopying technology or laser printer technology (which processes are elucidated in, for example, L.B. Schein, Electrophotography and

Development Physics, pages 32-244, Volume 14, Springer Series in Electrophysics 1988; the disclosure of which is incorporated herein by reference).

According to a preferred embodiment of the invention the powder paint particles are mixed with magnetic or non-magnetic carrier particles to obtain friction charging whereupon the mixture is transported and the powder paint particles are applied to the substrate or a transfer medium, and subsequently transfereed to the substrate, by means of an electric field between the substrate or the transfer medium and the means of transport.

Depending on the conductivity of the substrate the electric field between the substrate and the transfer medium or means of transport can be applied with suitable methods like for instance a corona discharge or a moving or fixed counterelectrode (see for instance Schein, pp. 36-37 and 47).

In case a transfer medium is used, the powder paint particles are first applied to the transfer medium by means of an electric field, transported to the substrate by the transfer medium and then applied to the substrate by, for example, electrical, electrostatic or mechanical forces. Thermal processes can also be used in this application step.

The present process allows powder paint particles to be applied to coated or uncoated board- or paper-like substrates such as, for example, cardboard, hardboard, fibre board for example MDF, particle board, chipboard, plywood, veneer, block board (which board products can be paperfaced), wood, timber and paper at rates up to, for instance, 400 meters of substrate/minute with a film thickness of the cured film of between, for example, 1 μm and 100 μm .

Preferably, the polymer having unsaturated groups has a molecular weight (M_n) between about 800 and about 6800 grams/mole and a viscosity between 1 dPas and

800 dPas (measured with an Emila rheometer at 165°C).

Preferred polymers are unsaturated polyesters, unsaturated polyacrylates and acrylated polyesters.

Preferably, the unsaturated polymer has a degree
5 of unsaturation between 300 and 1800 grams per mole of unsaturated group (WPU), a molecular weight (Mn) between about 800 and about 6800 and a viscosity between 1 dPas and 400 dPas. The preferred degree of unsaturation for an unsaturated polyester is between 500 and 1500 grams per
10 mole of unsaturated group.

The molecular weight (Mn) is preferably between about 2500 and about 4500 grams/mole.

The unsaturated polyester can be (semi)crystalline or amorphous.

15 In general, the glass transition temperature (Tg) of the amorphous resin is higher than 40°C. Semi-crystalline resins have a Tg and a melting point (Tm), and Tg is lower than Tm.

The melting point of the (semi)crystalline
20 unsaturated polyester is between about 40°C and about 180°C, and preferably, is between about 60°C and about 140°C. The melting point and the melting range are discussed at pages 36, 286 and 295 of Misev, Powder Coatings, Chemistry and Technology Wiley 1991, the
25 disclosure of which is incorporated herein by reference.

Thermosetting powder coatings that are based on unsaturated polyester are described in Misev, Powder Coatings, Chemistry and Technology, at pages 167-170, the disclosure of which is incorporated herein by reference.

30 Preparation of the unsaturated polyester can be carried out in a single-step process in which unsaturated polyfunctional carboxylic acids and glycols are heated to a temperature, for example, between about 180°C to about 230°C for between about 6 hours to about 15 hours.

35 Preparation of the unsaturated polyester can also be carried out in a two-step process in which saturated glycols and saturated polyfunctional carboxylic

acids are esterified in a first step at, for example, between about 230°C to about 250°C for between about 2 hours to about 8 hours. In a second step, saturated or unsaturated glycols and acids, or mixtures thereof, are esterified at, for example between about 180°C and 220°C for between about 2 to about 8 hours.

In general, the unsaturated polyester is obtainable from the condensation of one or more aliphatic or cycloaliphatic mono-, di- or polyfunctional alcohols, or mixtures thereof, one or more aliphatic, cycloaliphatic, or aromatic di- or polyfunctional carboxylic acids, or mixtures thereof, and if desired, a monofunctional carboxylic acid or the corresponding ester of this monofunctional carboxylic acid.

Examples of suitable alcohols and glycols include, among others, benzyl alcohol, ethylene glycol, propylene glycol, neopentylglycol, butanediol, hexanediol, dimethylol cyclohexane, diethylene glycol, glycerol, trimethylol propane, pentaerythritol, dipentaerythritol, or mixtures thereof. Instead of an alcohol or glycol, or together with an alcohol or glycol, one or more epoxy compounds such as, for example, ethylene oxide, propylene oxide, allyl glycidyl ether, or mixtures thereof, can be used.

Examples of suitable di- or polyfunctional carboxylic acids include maleic acid, fumaric acid, itaconic acid, citraconic acid, malonic acid, succinic acid, glutaric acid, adipic acid, sebacic acid, 1,4-cyclohexane dicarboxylic acid, hexahydrophthalic acid, hexachloroendomethylenetetrahydrophthalic acid, dichlorophthalic acid, isophthalic acid, terephthalic acid, trimellitic acid, or mixtures thereof.

Fumaric acid, maleic acid, or a mixture thereof, is preferred.

The carboxylic acids can also be applied in the corresponding anhydride form, so that, for example, tetrahydrophthalic anhydride, maleic anhydride, phthalic

anhydride, or mixtures thereof can be used.

If desired, the unsaturated polyester can also be obtained from saturated or unsaturated monofunctional carboxylic acids, or mixtures thereof. These
5 monofunctional carboxylic acids include, for example, synthetic or natural fatty acids having 2 to 36 carbon atoms. Corresponding esters of monofunctional alcohols such as glycerol are used for esterification. Examples of
10 suitable monofunctional carboxylic acids include, among others, lauric, stearic, oleic, linoleic, benzoic, acrylic, methacrylic acid, or mixtures thereof. The unsaturated polyester can also contain dicyclopentadiene.

If the unsaturated polyester is hydroxyl-functionalized, then the hydroxyl number of the polyester
15 is usually between about 18 mg KOH/gram of resin and about 75 mg KOH/gram of resin.

If the unsaturated polyester is acid-functionalized, the acid number is usually between about 18 mg KOH/gram of resin and about 75 mg KOH/gram of resin.
20 Suitable acrylate polymers include, for instance, acrylate polymers having several side chains containing unsaturated groups.

These polymers can be obtained by means of a two-step process. In the first step an acrylate polymer is
25 prepared by a conventional polymerization process, in which also a certain proportion of functional monomer is copolymerized to obtain a functionalized acrylate polymer. This functional monomer, which usually is present in amounts of between 3 and 60 wt. %, can be, for example, an
30 epoxy functionalized monomer such as glycidyl (meth)acrylate; an acid functionalized monomer such as, for instance, (meth)acrylic acid, a hydroxy functionalized monomer such as, for instance hydroxyethyl(meth)acrylate; or an isocyanate functionalized monomer such as, for
35 instance, TMI (meta-isopropenyl- α - α -dimethylbenzyl-isocyanate).

In the second step for the acrylate synthesis,

an addition reaction, is carried out between the functional groups of the acrylate polymer which is prepared in the first step and a compound having both a functional group capable of reacting with the functional groups and also an unsaturated group in the side chain.

For the addition reaction of this second step, the functionalized acrylate resin can be dissolved in a solvent such as for example toluene, xylene and/or butyl acetate. The compound having the unsaturated group, is added at temperatures between, for example, 50°C and 150°C and next, stirring takes place for some hours. Progress of the reaction can be monitored by means of titrations of, for instance, acid groups or isocyanate groups. Addition reactions of this second step are, for instance, between a compound having an acid group and an epoxy functional acrylate polymer, a compound having a hydroxyl group and an isocyanate functionalized acrylate polymer, a compound having an isocyanate group and a hydroxyl functionalized acrylate polymer, a compound having an anhydride group and a hydroxyl functionalized acrylate polymer or a compound having an epoxy group and an acid functionalized acrylate polymer.

It is preferred to allow an epoxy functionalized acrylate polymer to react with (meth)acrylic acid.

The unsaturated side chain can have, for example, methacrylate ester, allyl, vinyl, vinyl ether, or anhydride groups, or mixtures thereof. Suitable compounds that are allowed to react with the functionalized acrylate copolymer are, for example, methacrylic acid, glycidyl methacrylate, TMI, allylglycidyl ether, hydroxybutylvinyl ether, maleic anhydride, or mixtures thereof.

The unsaturated acrylate polymer can also be obtained by means of a multi-step process. For example, one of the isocyanate groups of a diisocyanate compound such as, for example, isophorone diisocyanate (IPDI), hexamethylene diisocyanate (HDI) or methylene-biscyclohexylisocyanate (hydrogenated MDI) is allowed to

react with a methacrylate monomer having the hydroxyl functionality. The resulting urethane compound, which contains isocyanate and methacrylate groups for further reaction, can subsequently be allowed to react with, for example, an acrylate copolymer having the hydroxyl functionality. This acrylate copolymer can be prepared using, for example, hydroxyethyl methacrylate as a functionalized monomer.

Depending on the binder system a crosslinker has to be applied or can optionally be applied.

A preferred crosslinking agent for the radiation curable binder composition according to the present invention is an oligomer or polymer having one or more vinyl ether, allyl, vinyl ester, or (meth)acrylate groups. More preferably an oligomer or polymer having at least two vinyl ether groups is applied.

The crosslinking agent having vinyl ether groups is preferably made of a divinyl ether functionalized urethane based on, for example, a diisocyanate and hydroxybutyl or hydroxyethyl vinyl ether.

Suitable crosslinking agent having (meth)acrylic groups include for example dimethacrylate functionalized urethane based on, for example, a diisocyanate and hydroxyethyl methacrylate or polymethacrylate functionalised urethanes.

Suitable difunctional isocyanates used in the preparation of the crosslinking agent include isophorone diisocyanate, or methylene diisocyanate, or methylenebiscyclohexylisocyanate. Functionalized oligomers derived from these diisocyanates such as isocyanurates, uretdiones, and biurets can, for example, also be used.

Preparation of vinyl ether functionalized diurethanes can be carried out by means of the process described in, for example, EP-A-505.803, the complete disclosure of which is incorporated herein by reference.

Preparation of suitable vinyl ether terminated ester oligomers for use as crosslinking agent is described

in WO-A-89/10.346, the complete disclosure of which is incorporated herein by reference. A suitable vinyl ester functional compound is, for example, divinyl adipate.

The crosslinking agent preferably contains
5 between about 1 to 10 vinyl groups, and more preferably, contains at least two vinyl groups per molecule.

The crosslinking agent can be a liquid or a solid. Solid crosslinking agents are preferred because good powder stability is more easily achieved, after
10 combination of the crosslinking agent with the unsaturated polymer.

The crosslinker having allyl groups can for example have 2-12 allyl groups. The crosslinker can have allylether groups and further ester or urethane groups.
15 The crosslinker can also have vinylether and allylether groups. It is also possible to use vinylether and allylether containing crosslinkers.

Very suitable crosslinkers include, for example, the ester of trimethylolpropane diallyl ether or
20 pentaerythritol triallyl ether and a polycarboxylic acid (anhydride). Also oligomers containing allyl groups, for example, allyl alcohol, trimethylolpropane diallyl ether, allyl glycidyl ethers and pentaerythritol triallyl ether. Examples of suitable isocyanates are isophorone
25 diisocyanate, toluene diisocyanate, hexamethylene diisocyanate and methylene biscyclohexylisocyanate.

The relative amounts of polymer having unsaturated groups and crosslinking agent in the binder composition depend in part on the choice of crosslinking
30 agent. In general, if the crosslinking agent is vinyl ether functionalized, the equivalent ratio of polymer unsaturation to crosslinking agent unsaturation is between 1:2 and about 2:1, and preferably, about 1:1. In general, if the crosslinking agent is a methacrylate or a vinyl
35 ester functionalized compound, the equivalent ratio of polymer unsaturation to crosslinking agent unsaturation is between about 1:2 and about 2:1, and preferably, about

1:1.3.

A suitable cationic curable system based on epoxy resins is disclosed in EP-A-667381.

Radiation curing is preferably carried out via
5 ultraviolet (UV) or electron beam (EB) curing. These techniques are described in, for example, the article, "UV and EB-curing", by S.J. Bett et al. in Jocca 1990 (11), pgs. 446-453, the complete disclosure of which is incorporated herein by reference. Most preferably UV-
10 curing is applied. Very suitable UV-lamps for curing thin layers or to obtain high speeds are excimer lamps (as described for example at pages 48-52 of the Conference Proceedings of RAD TECH Europe September 25, 1995, in Maastricht).

15 For UV-radiation curing of the powder paint formulation a photoinitiator is mixed with the binder composition at a temperature between, for example, about 50°C and about 150°C. Mixing can take place in a solvent or in the melt with use of an extruder, wherein the latter
20 is preferred. Pigments, flow promoters, other additives, or mixtures thereof, can also be used.

Another advantage of the present invention is the fast cure at lower temperatures, in comparison with the prior art processes related to thermocuring systems,
25 resulting in a lower thermal load on the substrate which is very relevant for the present substrates.

An important advantage of the radiation curing according to the present invention is that flow of the powder paint on exposure to heat is fully separated from
30 the curing reaction on exposure to UV or electron beam radiation, which enables powder coatings to be made that exhibit excellent flow.

Common additives such as, for example, pigments, fillers, flow promoters, tribo additives, stabilizers, or
35 mixtures thereof can be added to the binder system. Suitable pigments include, for example, inorganic pigments such as titanium dioxide, zinc sulphide or iron and

chromium oxide, and organic pigments such as, for example, azo compounds.

Suitable fillers include, for example, metal oxides, silicates, carbonates, sulfates, or mixtures thereof, as known to those skilled in the art.

The powder paint compositions can, for example, be prepared and characterized as described in, for example, the aforementioned Misev on pages 224-283 which disclosure is incorporated herein by reference. The selection of grinding, classifying and sieving equipment is important for obtaining the desired particle size of the powder paint particles. For this purpose target mills, fluidised bed mills, static classifiers and rotating classifiers may be used.

Upon curing or fusing of a powder paint composition a powder coating is obtained.

The median particle size (by volume) of the powder paint particles $X_{50,3}$ (as defined according to the description and notation at pages 12-14 of Mechanische Verfahrenstechnik by Prof. Rumpf (Carl Hansen Verlag, 1975)) can be, for example, below about 200 μm , and preferably, is between about 5 and about 60 μm .

The selection of the particle size depends on, for example, the desired final coating thickness for a given application.

The particle size distribution can be as broad as it is in conventional powder paint technology.

Preferably, the particle size distribution is relatively narrow. More preferably, the ratio $X_{75,3}:X_{25,3} < 3$ (according to the definition in the aforementioned Rumpf), since the efficiency of the development step may vary with the particle size.

It is one of the advantages of the process according to the present invention, that it is possible to apply particles having median particle sizes between about 5-30 μm . These particle sizes are very suitable to be applied for a clear varnish. It is very difficult to apply

particles of such a size with conventional spray guns.

Carrier particles can be either magnetic or non-magnetic. Preferably, the carrier particles are magnetic particles.

5 Suitable magnetic carrier particles have a core of, for example, iron, steel, nickel, magnetite, $\gamma\text{-Fe}_2\text{O}_3$, or certain ferrites such as for example CuZn, NiZn, MnZn and barium ferrites. These particles can be of various shapes, for example, irregular or regular shape.

10 Generally, these carrier particles have a median particle size between 20 and 700 μm . Preferably, the carrier particle size distribution is narrow and more preferably the ratio $X_{75,3}:X_{25,3} < 2$.

 Exemplary non-magnetic carrier particles include
15 glass, non-magnetic metal, polymer and ceramic material.

 Non-magnetic and magnetic carrier particles can have similar particle size.

 Preferably the carrier core particles are coated or surface treated with diverse organic or inorganic
20 materials to obtain, for example, desirable electrical, triboelectrical and/or mechanical properties. Inorganic materials are described in for example US-A-4925762 and US-A-5039587. Organic coating materials include, for example, polymers having fluor-, silicone-, acrylic-,
25 styrene-acrylic, melamine- or urethane-group. Mixtures of these polymers can also be used. Preferably a fluor containing polymer is used as coating.

 For coating the carrier particles, any suitable method to coat a thin or thick layer on a powder surface,
30 such as, for example spray coating in a fluidized bed or dry coating in a rotary kiln, can be used.

 The carrier coatings can comprise suitable fillers or additives to control for example, triboelectrical, electrical or mechanical properties of
35 the carrier coating. For example, conductive materials such as, carbon black and metal powder, or charge controlling material and flow improving materials can be

used.

The carrier particles may be conductive (as described in for example US-A-4076857) or non-conductive.

Preferably, carrier particles having high
5 voltage break through are used so that high electric fields can be used between the transport means and the substrate or the transfer medium to achieve a thick powder coating layer.

A developer comprises a mixture of powder paint
10 particles and carrier particles. A development method is a way of developing and a development unit is a complete system comprising of, for example, a developer roller (transport medium), mixing screw(s), a supply device, blades, detectors and the like. Suitable examples are
15 described in, for example, GB-A-2097701, US-A-4147127 and US-A-4131081.

In the present invention the development method can be either one-component or two-component. According to a preferred embodiment of the invention the two-component
20 development method, in which the carrier particles are mixed with the powder paint particles, is used. Alternatively, also all kinds of monocomponent development like, for example, magnetic conductive, magnetic insulative or non magnetic development as disclosed on
25 pages 203 ff of the above mentioned Schein or binary developers consisting of e.g. magnetic toner and carrier as described in US-A-5516613 can be used.

Preferably, a combination of powder paint particles having a $X_{50,3}$ below 80 μm and a $X_{95,3}$ below
30 120 μm and carrier particles having a $X_{50,3}$ below 180 μm and a $X_{95,3}$ below 200 μm is used.

More preferably, a combination of powder paint particles having a $X_{50,3}$ below 30 μm and above 5 μm and a
35 $X_{95,3}$ below 50 μm and carrier particles having a $X_{50,3}$ below 180 μm and above 5 μm and a $X_{95,3}$ below 200 μm is used.

In the two-component developer the amount of powder paint particles can be, for example, between about

1 and about 50 wt.% and preferably between about 5 and about 25 wt.% (relative to the amount of developer). It is an advantage of the process according to the invention that it is possible to use powder paint concentrations well in excess of 10 wt.%, which is usually not possible in printing applications. Consequently, the amount of carrier particles can be between about 50 and about 99% by weight (relative to the amount of developer) and preferably is between about 75 wt.% and about 95 wt.%.
5

10 The powder paint concentration can be externally or internally (in the development unit) controlled. External control can be effected by measurement of layer thickness of uncured or cured powder by, for example, optical, photothermal or dielectrical means. Internal control can be carried out in the developer station by means of powder paint concentration control by any suitable means like inductive control (see, for example, US-A-4147127 and US-A-4131081) or volume control.
15

In a two-component development method the powder paint particles are triboelectrically charged by intensive mixing and friction with the carrier particles.
20

In the process according to the present invention it is also possible to use a one component development method with the carrier particles being incorporated in the powder paint particles as disclosed in, for example, US-A-4803143 and US-A-4543312.
25

In a one-component development method the particles are charged by induction or friction, depending on the selection of the powder paint particles.

30 Both one- and two-component developers can be transported by magnetic, electric and/or mechanical transport.

Preferably, the means of transport is a conveying method.

35 The mixture is preferably conveyed by means of a magnetic roller as described in for example US-A-4460266. In addition to a magnetic brush apparatus also useful in

the present process are, for example, non-magnetic cascade development (see page 94 of the hereinbefore incorporated reference of L.B. Schein) and magnetic cascade development (as described in for example "The 9th International Congress on Advances in Non-Impact Printing Technologies/Japan Hardcopy '93, pages 133-140). In addition also transport by air, for example, powder cloud development can be used. An exemplary process is described in for example US-A-2725304. Also jumping (projection) development (see for example Electrophotography, Fourth International Conference, pages 207-228, Nov. 16-18, 1981) can be carried out.

When two-component developers are used, the parameters which are relevant for the process (such as, for example, powder paint concentration, development potential and machine parameters) can be chosen depending on the application. This may lead to batch developer replacement, e.g. after certain time intervals or if certain parameters are out of a control range. Preferably, continuous developer material replenishment, as described in, for example, US-A-4614165, can be used to avoid process interruption for batch replenishment.

The substrate can have any desired shape such as band or sheet, i.e. continuous or discontinuous.

If a transfer medium is used between the transport means and the substrate any suitable transfer medium like, for example, metallic drums, dielectric drums, foil from metals or polymers like silicone rubber, as described in "Proceeding of IS&T's Seventh International Congress on Advances in Non Impact Printing Technologies", Vol. II, page 453-462, a web as disclosed in EP-A-332223, or composite materials can be used.

Alternatively a two step transfer may be used in which a layer of powder paint is developed on a first transfer medium and then transferred to a second transfer medium and finally transferred to the substrate.

The present coating process can be

advantageously used in the application of varnishes. Surprisingly, it was found that fully closed layers having a thickness of about 5 μm can easily be obtained with the process according to the invention whereas it is very
5 difficult to obtain such layers with spraying techniques.

Generally, more layers can be applied with or without intermediate fusing separately on the substrate or separately on the transfer medium and jointly transferred to the substrate.

10 A preferred process according to the present invention thus comprises charging of the powder paint particles by intensive mixing and friction with magnetic carrier particles, transport of carrier particles and powder paint particles with the aid of a magnetic roller
15 and subsequent application of the powder paint particles to a substrate or a transfer medium, and subsequently transferred to the substrate, by means of an electric field between the substrate or the transfer medium and the magnetic roller, whereafter the powder paint composition
20 is cured or fused to a powder coating using techniques known in the art.

For melting, the applied powder paint can be transferred into an oven or can be exposed to IR radiation, or a combination of both. Alternatively all
25 other suitable fusing methods e.g. as disclosed on page 47-49 of the above mentioned Schein can be used. The applied powder paint is molten at temperatures between, for example, about 60°C and about 140°C to form a continuous, smooth, softened or molten coating with
30 coating thickness between, for example, about 1 μm and about 100 μm . Then, the hot panel is cured with use of a UV light source. Post-heating can also be carried out. The powder coating adheres to the substrate.

It is possible to apply the coating on printed
35 substrates produced with common printing techniques (offset, gravure, flexo, digital printing either electrographic or inkjet). The printing process and the

coating process can be carried out in two separate steps (off-line) or as well in one production step (on-line).

The coating may cover the full area of the substrate or only part of it (spot coating). In case of spot coating any image creating technology as described in the above mentioned Schein may be used to create an image on a suitable transfer medium or as first transfer medium in case of two step transfer as described before.

The carrier particles may be metered to a mixing arrangement in which, one or more means of intensive mixing such as, for example, worm wheels are present along with a magnetic roller. Suitable mixing arrangements are described in, for example, "Proceeding of IS&T's Seventh International Congress on "Advances in Non Impact Printing Technologies", Vol. 1, pages 259-265, the complete disclosure of which is herein incorporated by reference.

Next, an amount of powder paint particle is fed into the mixing arrangement which is selected so as to obtain a powder paint particles concentration of, for example, about 5-25 wt.% powder paint relative to the amount of carrier particles. In this way, a developer is formed.

During the intensive mixing and friction in the mixing arrangement, due to the action of the worm weels, the carrier particles and the powder paint particles become oppositely (tribo) electrically charged. A layer of electrically charged powder paint particles covers the carrier particles. The carrier particles subsequently act as carrier for the charged powder paint particles. Next, the developer is fed to the magnetic roller, on which a brush-like structure, also known as the magnetic brush, is formed. The magnetic roller transports the brush to the contact area with the substrate or transfer medium. In this way, powder paint particles, as well as carrier particles, become available at the contact area with the substrate or transfer medium. By applying a sufficiently strong electric field between the magnetic roller and the

substrate or transfer medium the powder paint particles can be drawn from the brush to the substrate or transfer medium, onto which they adhere electrostatically. In the case a transfer medium is used, the powder paint particles
5 are subsequently transported to the contact area of the transfer medium and the substrate and next transferred to the substrate by means of one of the aforementioned transfer processes.

Finally, the magnetic brush is scraped off the
10 magnetic roller as it is returned into the mixing bin.

As a result, a layer of powder paint particles forms on the substrate, which layer is substantially free from carrier particles, and can then be cured. Eventually, an apparatus which can catch carrier particles can be
15 introduced such as for example a catching equipment for residual carrier, as described in "Proceeding of IS&T Eighth International Congress on Advances in Non Impact Printing Technologies", pages 391-393. The thickness of said layer of powder paint particles can, for example, be
20 controlled via the electric field strength between the magnetic roller and the substrate, or the transfer medium, the magnitude of the charge on the powder paint particles (e.g. by varying the concentration and the mixing time) and the roller speed.

25 The process according to the invention can advantageously be applied in equipment for small-scale application of overprint varnishes. These machines can be used online or offline in connection with black and white, two colour or full colour copy machines or computer output
30 printers to produce paper or cardboard sheets with high gloss and high resistance e.g. against fingerprints, oil and acids. The process may be used as an alternative to lamination.

The process can also be used in-line or off-line
35 in connection with printing machines of any speed and any technology (for example large scale) like offset, gravure, flexo or digital printing to produce overprint varnishes

e.g. for cover sheets of booklets and printed cardboard for packaging.

5 The process may be used for varnishes, which may be applied below or above a tonerbased image to improve adhesion of the toner to the paper and to improve protection against, for instance, falsification of a document.

10 The development station with toner hopper and optional the transfer means and the fusing and curing means may be designed in a way that it can be easily interchanged, for instance as a cartridge, by any (unskilled) person, for example, for use in a copying machine or laser printer. Consequently, these small scale overprint varnish application machines can be used, for
15 example, in printing shops, copy shops and offices.

The invention will be further described based on the following non-limiting examples.

Examples

20

Example I

Preparation of powder paint composition I

25 A powder paint composition was prepared by premixing 830 parts by weight of a polyester resin (Uralac XP3125 of DSM Resins), 170 parts by weight of a crosslinker (Uralac ZW 3307 of DSM Resins), 10 parts by weight of photoinitiator (Irgacure 184™) and 6 parts by weight of flow agent (Byk 361™) in a Henschel batch mixer and next melt kneaded in a Buss-Ko-Kneader PLK 46.

30

The cooled extrudate was milled first in a hammer mill to a particle size < 3mm and then fed into a target mill (NPK Labojet) obtaining a powder paint with a medium particle size of 10.8 µm and a $d_{75,3}/d_{25,3}$ ratio of 3.3.

35

Example IIPreparation of a carrier

998 parts by weight Cu-Zn-ferrite powder, having a median particle size of 81 μm and a ratio $X_{75,3}/X_{25,3}$ of 1,32 (both measured with the laser granulometer Cilas HR 850), were dry coated with 2 parts by weight polyvinylidenedifluoride (Kynar 301F[™]) by mixing both materials in a Lödige mixer and coating the polymer on the surface of the ferrite in a rotary kiln at 200°C under N₂-atmosphere to obtain a carrier with a medium size of 80 μm , a ratio $X_{75,3}/X_{25,3}$ of 1.32, a resistance of $1.1 \cdot 10^{10}$ Ohm at a potential of 10V and a break-through voltage above 1,000V (both measured in a c-meter of Epping GmbH).

15 Example IIIPreparation of developer I

16% by weight of the powder paint composition according to Example I and 84% by weight of the carrier according to Example II were mixed at room temperature intensively in a "Skandex" paint shaker for 5 minutes to obtain a developer. The charge distribution of the developer was measured in a q-meter of Epping GmbH showing a narrow charge over diameter (q/d)-distribution with a median of 2.2 fC/10 μm , a standard deviation of 1.7 fC/10 μm and 5.2% oppositely charged particles.

Example IVCoating on a substrate

The developer according to Example III was filled in a magnetic brush unit mounted in a distance of 2.5 mm of a rotating metal drum available as the ld-tester (developer life time tester) from Epping GmbH. On the rotating drum a cardboard substrate of 0.3 mm thickness preprinted with red offset printing ink was mounted. The rotation speed of the drum (i.e. coating speed) was 30 m/minute, and the speed of the magnetic brush was 78 meters/minute in the same direction as the drum. The

doctor blade of the magnetic brush was adjusted to a distance of 1.5 mm to the magnetic roller. The magnetic pole was adjusted -10 degrees compared to the line between both rotating axes. The development potential of the drum
5 against the developer roller was set to the following values (Table I):

TABLE I

10	development voltage	average coating layer thickness	coating properties
	-1000 V	7.5 μm	high gloss (97%), closed film, oil-and tensid tight
	-800 V	3.5 μm	high gloss (94%), closed film, oil-and tensid tight
	-600 V	2.5 μm	medium gloss (75%)
15	-400 V	1.5 μm	low gloss (38%)
	-200 V	1 μm	slight gloss (19%)

After application on the cardboard substrate, the powder
20 was heated at 70°C by means of IR to obtain a good flowing film, followed by a UV radiation treatment (1000mJ/cm²). The result in the examples of the first two blocks of Table I is a chemical resistant, hard and scratch resistant coating.

25 The gloss was measured with a Reflectometer supplied by Dr. Lange at 60° detection angle (according to DIN 67530).

Example VPreparation of powder paint II

99.5 parts by weight of the powder paint composition of Example I were mixed with 0.5 parts of weight of siliciumdioxide (Aerosil R504™) in a Henschel batch mixer at maximum speed for 3 minutes to achieve a powder paint II with excellent powder flow behaviour.

Example VI10 Preparation of powder paint III

99.5 parts by weight of the powder paint composition of Example I were mixed with 0.5 parts of weight of titaniumdioxide (Aerosil P25™) in a Henschel batch mixer at maximum speed for 3 minutes to achieve powder paint III with excellent powder flow behaviour.

Example VIIPreparation of developer II

11 parts by weight of the powder paint composition II according to Example V and 89 parts by weight of the carrier according to Example II were mixed in a "Skandex" paint shaker for 5 minutes to obtain a non-dusting developer II.

25 Example VIIIPreparation of developer III

15 parts by weight of the powder paint composition III according to Example VI and 85% by weight of the carrier according to example II were mixed in a "Skandex" paint shaker for 5 minutes to obtain a non-dusting developer III.

Example IXCoating a substrate

35 Analogous to Example IV the developer II according to Example VII and the developer III according Example VIII were used to produce a chemical resistant,

hard and scratch resistant coating on 0.3 mm thick cardboard preprinted with red offset ink (see Table II).

TABLE II

5		development voltage	average coating layer thickness	coating properties
	developer II	-1000V	7.6 μm	medium gloss (55-60%), closed film, oil and tensid tight
	developer III	-1000V	9.7 μm	high gloss (80-85%), closed film, oil and tensid tight

10

Example XPreparation of a powderpaint IV

The cooled extrudate from Example I was milled first in a hammer mill to a particle size <3 mm and then fed into a fluidized bed mill (Condux CFS8), having a nozzle diameter of 4 mm. The material was milled with 6 bar overpressure at 3800 r.p.m. of the classifier wheel incorporated in the mill and after that fed into a separate classifier (Condux CGS16) at 8000 r.p.m. of the classifier wheel to reduce the fraction of fine particles below 5 μm in the powder obtaining a powder with a median particle size of 13.7 μm and a ratio $X_{75.3}/X_{25.3}$ ratio of 2.3. 99.5 parts by weight of this powder were mixed with 0.5 parts of weight of titaniumdioxide (Aerosil P25™) in a Henschel batch mixer at maximum speed for 3 minutes to achieve powder paint IV with excellent powder flow behaviour.

Example XIPreparation of developer IV

10 parts by weight of the powder paint according to Example X and 90% by weight of the carrier according to example II were mixed in a "Skandex" paint shaker for 5 minutes to obtain a non-dusting developer IV.

Example XIICoating a substrate

10 Analogous to example IX the developer IV according to Example XI was used to produce a 7.5 μm thick coating on a 90 g/m² paper preprinted in a commercially available dry toner based 4 colour copier/printer. The coating was proven to be hard and chemical, scratch
15 and fingerprint resistant. The coated sheets were medium glossy (60-70%). The protection of prints against falsification were improved as any damage of the surface can easily be detected by the change of gloss of the surface.

20

C L A I M S

1. A process for coating a board- or paper-like
5 substrate with a powder paint composition, characterized in that powder paint particles are first charged by friction or induction in the presence of magnetic or non-magnetic particles, are next transported and are then applied to the
10 substrate or applied to a transfer medium, and are then subsequently transferred to the substrate, by means of an electric field between the substrate respectively the transfer medium and the means of transport, whereafter the powder paint composition is
15 fused and cured to a powder coating wherein the powder paint particles are based on solid particles of a radiation curable binder.
2. A process according to Claim 1 characterised in that the radiation curable binder comprises a polymer
20 having unsaturated groups.
3. A process according to any one of Claims 1-2, characterized in that the substrate is cardboard, hardboard, fibre board, particle board, chip board, plywood, veneer, block board, wood, timber or paper.
- 25 4. A process according to any of Claims 1-3, characterized in that the substrate is cardboard or paper.
5. A process according to any one Claims 1-4, characterized in that the powder paint particles are
30 mixed with magnetic or non-magnetic carrier particles to obtain friction charging whereupon the mixture is transported and the powder paint particles are applied to the substrate by means of an electric field between the substrate and the means of
35 transport.
6. A process according to any one of Claims 1-5, characterized in that the powder paint particles have

- a $X_{50,3}$ below 80 μm and a $X_{95,3}$ below 120 μm .
7. A process according to any one of Claims 1-6, characterized in that the powder paint particles have a $X_{50,3}$ below 30 μm and above 5 μm and a $X_{95,3}$ below 50 μm .
8. A process according to any one of Claims 1-7, characterized in that the carrier particles have a $X_{50,3}$ below 180 μm and above 5 μm and a $X_{95,3}$ below 200 μm .
9. A process according to any one of Claims 1-8, characterized in that the magnetic or non-magnetic carrier particles are selected from magnetic carrier particles consisting of a core of iron, steel, nickel, magnetite, $\gamma\text{-Fe}_2\text{O}_3$, or ferrites or non-magnetic carrier particles including glass, non-magnetic metal, polymer and ceramic material.
10. A process according to any one of Claims 1-9, characterized in that the process comprises charging of the powder paint particles by intensive mixing and friction with magnetic carrier particles, transport of carrier particles and powder paint particles with the aid of a magnetic roller and subsequent application of the powder paint particles to the substrate or to a transfer medium by means of an electric field between the substrate and the magnetic roller, whereafter the powder paint composition is cured or fused to a powder coating.
11. A two component developer comprising 1-50 % by weight powder paint composition as described in any one of Claims 1-10 relative to the developer.
12. A developer comprising carrier particles as described in any one of Claims 1-11 and powder paint particles.
13. Use of a radiation curable binder system in a process according to any one of Claims 1-10 or in a developer according to any one of Claims 11-12.
14. Use of a process according to any one of Claims 1-10 in the application of overprint varnishes.

15. Coated board- or paper-like substrate wherein the coating is obtained from a process according to any one of Claims 1-10.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/NL 97/00149

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 D21H19/00 D21H23/50 B05D1/00 B05D7/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 D21H B05D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	TAPPI, vol. 38, no. 10, October 1955, NEW YORK, US, pages 607-609, XP000600755 R.B.REIF: "An electrostatic process for applying dry coatings on paper" see the whole document	1-4, 15
A	US 5 039 587 A (CZECH ERWIN ET AL) 13 August 1991 cited in the application	
A	US 4 076 857 A (KASPER GEORGE PHILIP ET AL) 28 February 1978 cited in the application	
A	GB 2 055 619 A (BLUNDELL PERMOGLAZE LTD) 11 March 1981	
	--- -/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

7 July 1997

Date of mailing of the international search report

1 8. 07. 97

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+ 31-70) 340-3016

Authorized officer

Songy, 0

INTERNATIONAL SEARCH REPORT

International Application No
PCT/NL 97/00149

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 2 056 885 A (BLUNDELL PERMOGLAZE LTD) 25 March 1981 cited in the application -----	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/NL 97/00149

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5039587 A	13-08-91	DE 3831091 A CA 1320109 A EP 0359041 A JP 2114270 A PT 91694 B	29-03-90 13-07-93 21-03-90 26-04-90 31-05-95
US 4076857 A	28-02-78	AU 504743 B AU 2649877 A BE 856199 A CA 1064335 A DE 2729145 A FR 2356979 A GB 1549133 A JP 53003337 A NL 7706521 A,B,	25-10-79 04-01-79 28-12-77 16-10-79 29-12-77 27-01-78 01-08-79 13-01-78 30-12-77
GB 2055619 A	11-03-81	GB 2056885 A	25-03-81
GB 2056885 A	25-03-81	GB 2055619 A	11-03-81